

Screening Sediments from Marsh Creek, Saint John, New Brunswick for aromatic hydrocarbons

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ABSTRACT

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Sediment samples from an area heavily contaminated in the past by creosote were screened by extraction with dichloromethane and examination of the extracts by UV and visible spectrophotometry. Concentrations of dichloromethane extracts ranged from 0.7 to 287 mg/g dry sediment and the concentrations of their hexane-insoluble fractions from not detectable to 122 mg/g. Judging from UV spectra, parent PAHs were prevalent only in a few extracts. The spectra of these extracts could be approximated by spectra of mixtures of naphthalene, phenanthrene, fluoranthene, pyrene, and diesel oil. Spectra of the majority of extracts were relatively featureless and could be better approximated by the spectrum of bunker C oil. The described method is suitable to screen a large number of samples. Effluent from interceptor wells located at a retaining wall, constructed to retain creosote, contains creosote-related hydrocarbons at about 2 mg/L, some phenols, and a tentatively identified polyester resin, probably related to engineering plastics used in the wall construction.

RÉSUMÉ

Zitko, V. 2000. Screening sediments from Marsh Creek, Saint John, New Brunswick for aromatic hydrocarbons. Can. Tech. Rep. Fish. Aquat. Sci. 2307: iii + 31 p.

Des échantillons de sédiments d'un secteur auparavant fortement contaminé par la créosote ont été tamisés par extraction au dichlorométhane, et les extraits ont été examinés par spectrophotométrie dans l'UV et dans le spectre visible. Les concentrations des extraits de dichlorométhane allaient de 0,7 à 287 mg/g de sédiments secs tandis que les concentrations de leurs fractions d'hexanes insolubles allaient de non détectables à 122 mg/g. D'après les spectres dans l'UV, les HAP parents ne se trouvaient que dans quelques extraits. Les spectres de ces extraits pouvaient approximer ceux des mélanges de naphthalène, de phénanthrène, de fluoranthène, de pyrène et de carburant diesel. Les spectres de la majorité des extraits étaient relativement sans caractéristiques spéciales et pouvaient approximer celui du mazout brut. La méthode décrite convient à l'examen d'un grand nombre d'échantillons. Les effluents de puits d'interception à côté d'un mur de soutènement construit pour retenir la créosote contiennent des hydrocarbures liés à la créosote à environ 2 mg/L, des phénols et une résine polyester identifiée provisoirement, sans doute liée aux plastiques industriels qui sont entrés dans la construction du mur.

INTRODUCTION

The method of choice for the determination of hydrocarbons in sediments is gas chromatography-mass spectrometry, followed by high performance liquid chromatography with spectrophotometric (diode array) detection, the latter applicable when only aromatic hydrocarbons are of interest. These methods are relatively expensive and, because of their high sensitivity, require considerable dilution when presented with highly contaminated samples. In addition, the samples have to be carefully cleaned up, which lengthens the duration of the analysis. It is therefore of interest to examine the potential of other, faster and cheaper techniques, that could serve as screens for a preliminary examination of the extent of contamination and for the selection of samples that need to be analyzed in more detail. In addition, because of the heterogeneity of sediments, it may be of advantage to have a large number of screened samples rather than a small number of samples analyzed in detail. A similar idea, based on thin layer chromatography (TLC) and fluorescence spectrophotometry, has been suggested years ago (Hellmann 1975). Considering the level of PAHs in Marsh Creek sediment, fluorescence spectrophotometry is too sensitive as well.

This report describes the results of the screening of sediments from Marsh Creek by ultraviolet (UV) and visible spectrophotometry of dichloromethane extracts. Marsh Creek is a small stream in Saint John, New Brunswick, and contains an area contaminated heavily with creosote-type products (Leger and Drake 1998; Jacques Whitford Environment Limited 1998). A wood-preserving plant was formerly located on an adjacent Canada Post Corporation property.

A retaining wall, 'Waterloo barrier', was built along the Canada Post Corporation property in late 1998 to eliminate the movement of creosote from the property into Marsh Creek. Results of the analysis of the effluent from interceptor wells of this wall are also presented.

MATERIALS AND METHODS

Frozen samples of sediments from Marsh Creek were provided by ACAP Saint John in the fall of 1998. A map indicating the sampling locations is in the Appendix. The samples were thawed, aliquots were freeze-dried, sieved through a 0.5-mm sieve, and the loss on ignition at 550°C was determined. Subsamples (1.0 g) were placed on a layer of sodium sulfate (2 g) in a glass column (30 x 1.1 cm), and extracted by dichloromethane (15 mL). Dichloromethane was evaporated on a rotary

evaporator and the residue was weighed. The residue was then extracted with spectrograde hexane, the extract made to volume, diluted as necessary, and its UV spectrum was recorded in a 1-cm cell. A hexane-insoluble residue, referred to as 'bitumen', remained in some samples. The residue was weighed, dissolved in dichloromethane and the spectrum of the solution was also recorded.

Two water samples from Marsh Creek, and a sample of effluent (2.5 L) from interceptor wells of the retaining wall, were provided by ACAP Saint John on October 7, 1998, and on October 13, 1999, respectively. UV spectra of the samples were recorded and the samples were extracted with dichloromethane (50 mL) on magnetic stirrers for 2 h. The extracts of Marsh Creek water were evaporated to 3 mL and their spectra were recorded. The extract of the interceptor wells' effluent was dried by sodium sulfate, evaporated to dryness on a rotary evaporator and weighed. The residue was then extracted with hexane and the UV spectrum was recorded. The extraction left a hexane-insoluble residue, which was examined by infrared spectrophotometry (IR). The effluent was then acidified to pH=2 by concentrated hydrochloric acid, and the extraction procedure was repeated. The extracted effluent was neutralized by 50% sodium hydroxide and evaporated on a rotary evaporator to 50 mL. The concentrate was dialyzed through membrane tubing with molecular weight cutoff of 1000 dalton (SpectraPor CE membrane, Spectrum Medical Industries, CA, USA). A precipitate formed on dialysis and the non-dialyzable supernatant were freeze-dried and their IR spectra were recorded. An 'interphase' formed during the first dichloromethane extraction of the effluent was dried in the air and then over phosphorus pentoxide in vacuum before recording its IR spectrum.

Both hexane extracts of the interceptor wells' effluent were examined by thin layer chromatography (TLC) on Whatman Silica Gel 150A K5F 20 x 5 cm plates developed in either hexane, benzene, or petroleum ether-diethyl ether-glacial acetic acid 80:20:1 (v/v). The spots were visualized by UV absorbance, fluorescence, reaction with silver nitrate, charring with 60% sulfuric acid, and reaction with Fast Black K salt (FBK, Ojanperä et al. 1990).

Difference spectrum of basic (pH=10) minus acidic (pH=2) effluent was obtained by recording spectra of subsamples, prepared by adding three drops of 50% sodium hydroxide and of concentrated hydrochloric acid, respectively, to 20-mL aliquots of the sample. Maxima in the difference spectra may indicate the presence of phenols.

An HP 8452A diode array spectrophotometer with 2-nm resolution was used to record the UV/visible spectra. A Perkin-Elmer Model 700 IR spectrophotometer was used to record the IR spectra of samples in potassium bromide pellets.

PAH standards were products of Eastman Organic Chemicals, Marine Grade Creosote was supplied by Koppers Company, Organic Materials Division, Pittsburgh, PA 15219, and diesel fuel oil was obtained from the supply of the Biological Station. Bunker C was obtained several years ago from Imperial Oil.

Matlab (The MathWorks Inc., Natick, MA 01760, USA) was used to calculate the spectral approximations by the least squares technique, according to the equations

Proportions = Standards \ Spectra

and

**Approximated spectra =
Standards * Proportions,**

where

Proportions, Standards, Spectra, and Approximated spectra are matrices with the dimensions [components, samples], [wavelengths, components], [wavelengths, samples], and [wavelengths, samples], respectively, and '\ ' and '*' are the Matlab least squares and matrix multiplication operators, respectively.

RESULTS AND DISCUSSION

MARSH CREEK SEDIMENTS

The weight of a dichloromethane extract (DCE) is a good indicator of the degree of contamination (Table 1). The loss on ignition could also be used, but it is less specific than DCE. A further characterization of the DCE is provided by its UV spectrum (Fig. 1-6, arranged in order of increasing absorbance). UV spectra of extracts containing considerable concentrations of PAHs are conspicuous by the presence of one or several relatively sharp absorption maxima. In three samples (Fig. 5-6, samples 16, 28 and 32) the resemblance was so close that the concentration of creosote was also calculated and, in two cases, the result was in a reasonably good agreement with the concentration of DCE (Table 1).

Table 1. Contamination of Marsh Creek sediments. All results are based on dry weight of sediments

Sample	Dichloromethane extract, mg/g	As creosote mg/g	Bitumen mg/g	Loss on ignition, %
1	5.96		nd	7.87
2	6.06		nd	7.24
4	9.43		nd	11.67
6	7.39		nd	11.87
9	5.02		nd	6.66
10	13.56		0.3	10.67
12	9.52		nd	12.43
13	32.41		3.9	12.64
15	9.27, 8.15		nd	8.85, 9.03
16	286.24	323	122	28.07, 37.36
18	7.20		0.6	8.46
21	10.84		0.4	21.92
24	21.45, 22.66		0.2	17.26, 15.85
25	12.39		1.8	10.85
27	11.91		0.4	11.62
28	23.55, 15.56	20	1.9	8.15, 9.32
31	8.28		0.7	6.9
32	7.01, 16.49	3.6	1.9, 0.8	5.69, 5.69
34	5.98		0.2	4.98
35	0.66		nd	3.57

Spectra of the bitumens are reproduced in Fig. 7-11 for a wavelength range 240-400 nm, and in Fig. 12-16 for wavelengths from 350 to 700 nm. The former are practically featureless and show almost linear increases of absorbance with decreasing wavelength. The only exception is the spectrum of sample 16, which contains pronounced absorption maxima at 292, 324, 342, 358, and 378 nm (Fig. 11). Many of the visible spectra show signs of the presence of chlorophyll or its decomposition products, as a shoulder or a maximum at 412 nm and weak maxima at 666 or 582 nm.

It is obvious from the UV spectra that only in samples 16, 28, and 32, parent PAHs are significant components of the dichloromethane extracts. These spectra can be quite well approximated by spectra of a mixture of naphthalene, phenanthrene, fluoranthene, pyrene, and diesel oil, as shown in Fig. 17 and 18 for samples 16 and 32, respectively. The proportions of these hydrocarbons approximating all spectra are shown in Fig. 19; however, the mostly 'featureless' spectra can be better approximated by Bunker C alone, as demonstrated in Fig. 20 for sample 1. The substantial presence of other hydrocarbons is likely to limit the bioavailability of PAHs by retaining PAHs in the hydrocarbon phase (see, for example, Krasnochekova and Gubergits 1980). The absorption maxima of the UV spectra indicate that the major PAH is phenanthrene (reported UV absorption maximum at 252 nm, see, for example, Dabestani and Ivanov 1999). Freeze-drying of sediments may cause considerable losses of naphthalene (UV absorption maximum 221 nm). Crystals of naphthalene were recovered from the freeze-drier cooling coil after drying sample 16.

INTERCEPTOR WELLS' EFFLUENT

UV spectrum of the sample, as well as the spectra of two water samples from Marsh Creek, for reference, are presented in Fig. 21. A possible presence of phenols was indicated by a maximum around 270 nm (Fig. 22). Dichloromethane extract yielded 5.92 mg of residue, of which 1.96 mg was insoluble in hexane. The extraction of the acidified effluent yielded an additional 4.09 mg of extract, whose hexane-insoluble part was 2.48 mg.

UV spectrum of the first hexane extract (Fig. 23) indicates the predominance of naphthalene (maximum at 222 nm). The spectrum of the second hexane extract is similar to the spectra of most of the sediment extracts.

The IR spectra of the hexane-insoluble fractions indicate a polyester resin in the first, and a silicate, containing a small amount of an organic material, in the second extraction residue, respectively (Fig. 24, 25). Both materials are probably from some engineering plastics used in the retaining wall.

IR spectra of the high-molecular weight fractions of the effluent (Fig. 26) are typical of natural organic matter (NOM) such as humic (insoluble) and fulvic (soluble) acid. Their presence indicates surface (as opposed to ground) water.

On TLC, many of the spots are highly fluorescent, as expected from PAH-containing materials. Some phenols (spots on TLC detected by FBK) are present in much higher proportions than in the #16 Marsh Creek sediment (Fig. 27, middle sample), or in marine creosote (not shown).

CONCLUSIONS

Dichloromethane extraction of sediment and UV spectra of the extracts are useful for a rapid and inexpensive screening of sediment samples for hydrocarbon contamination.

Marsh Creek sediment at station 16 consists of almost 30% creosote. A complex mixture of hydrocarbons, somewhat resembling bunker C oil is present in other samples. Spectrum of the extract of Marsh Creek water, collected in 1998 downstream from the contaminated area was similar to the spectrum of bunker C oil.

UV spectra of three relatively creosote-rich extracts can be well approximated by spectra of mixtures of naphthalene, phenanthrene, fluoranthene, pyrene, and diesel oil, with diesel oil being by far the most predominant component, followed by phenanthrene. The majority of the spectra was relatively featureless and could be best approximated by a spectrum of bunker C oil.

The interceptor wells' effluent sample contains a variety of organic compounds, not all of them related to creosote. An overall impression is that the effluent is generated by surface water contacting an up till now fairly intact pool of creosote. Engineering plastics from the retaining wall construction seem to be adding additional organics. More samples should be analyzed to reach more definitive conclusions.

ACKNOWLEDGMENTS

Messrs. George Lindsay (Environment Canada) and Sean Brilliant (ACAP Saint John) commented on the manuscript. Ms. Marilyn Rudi edited and Ms. Brenda Best formatted the report.

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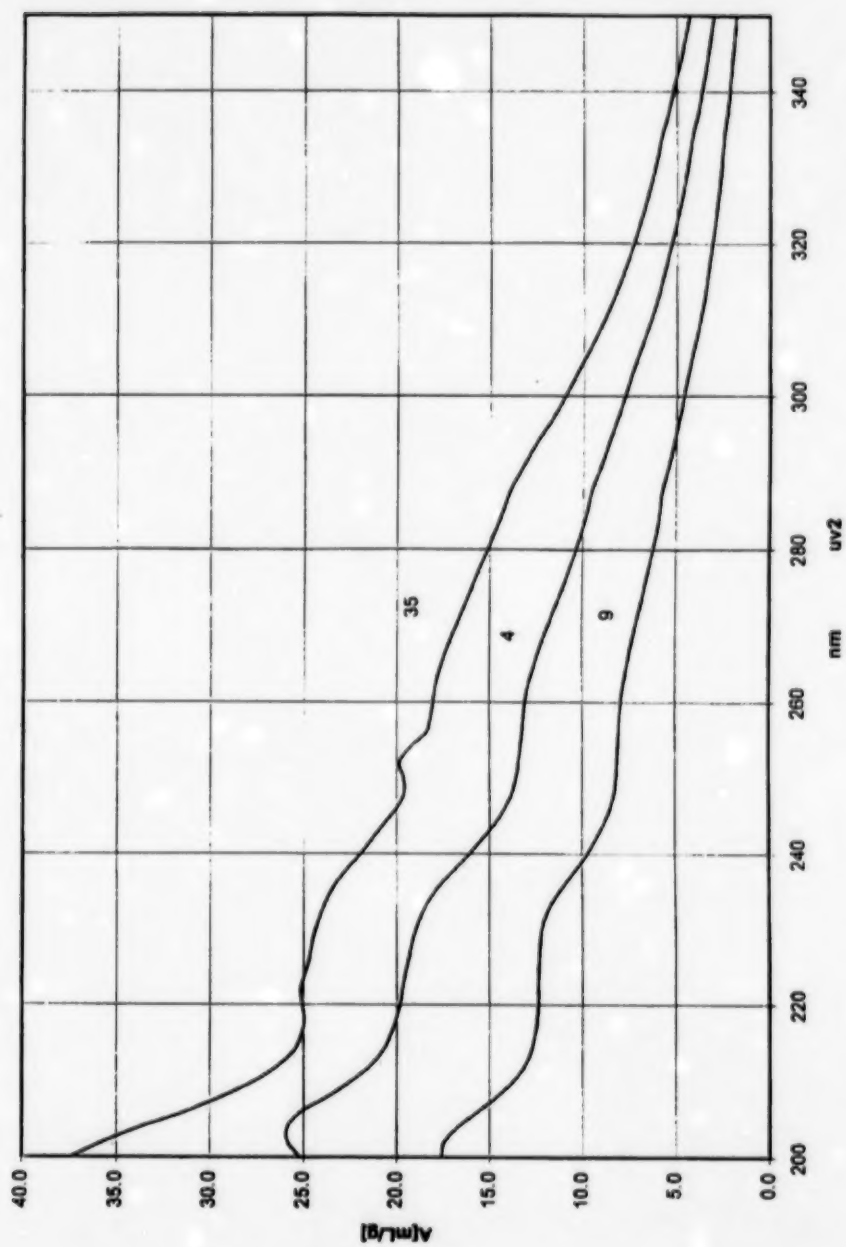


Fig. 1. UV spectra of hexane-soluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table I for sample characteristics and Appendix for sample locations.

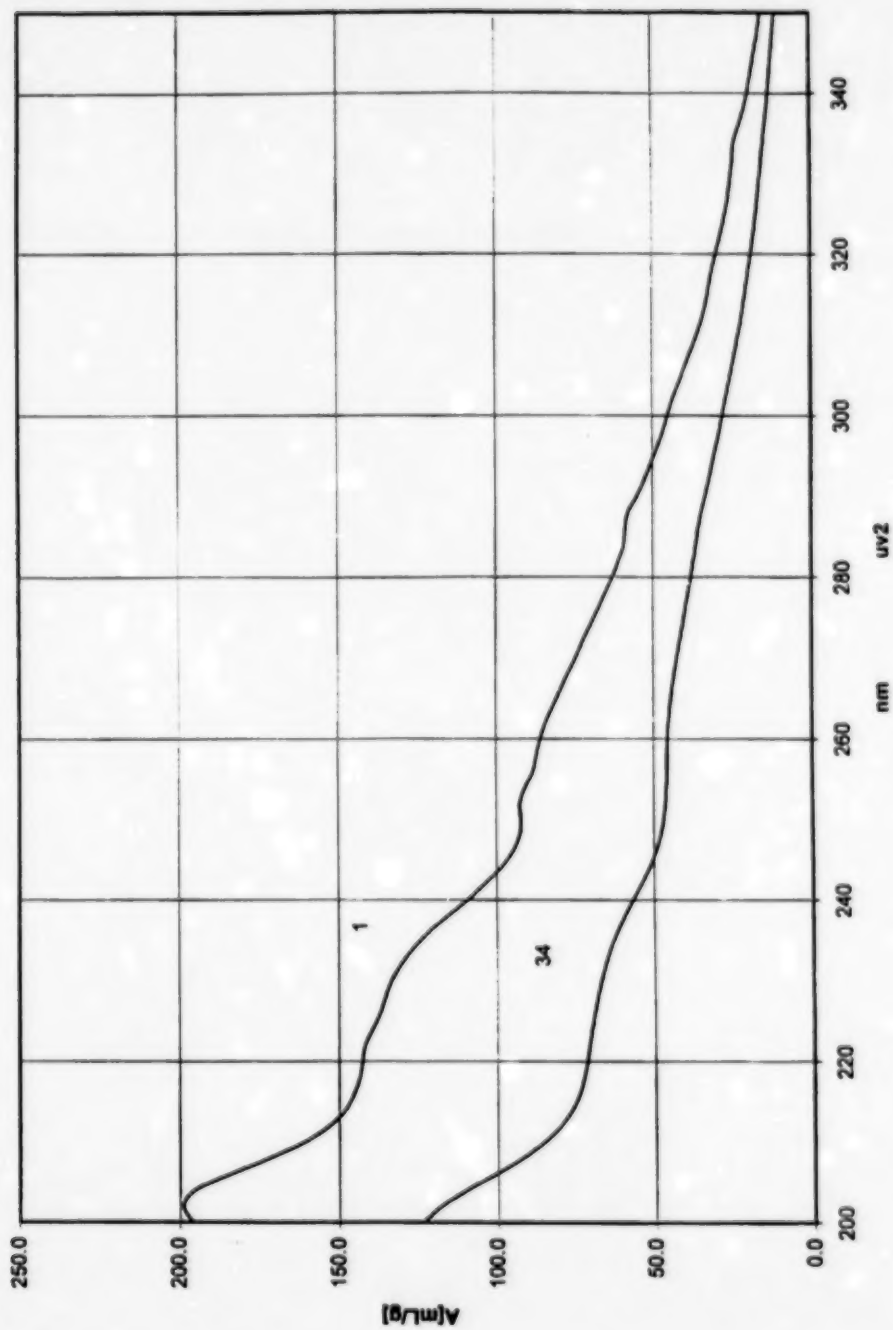


Fig. 2. UV spectra of hexane-soluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

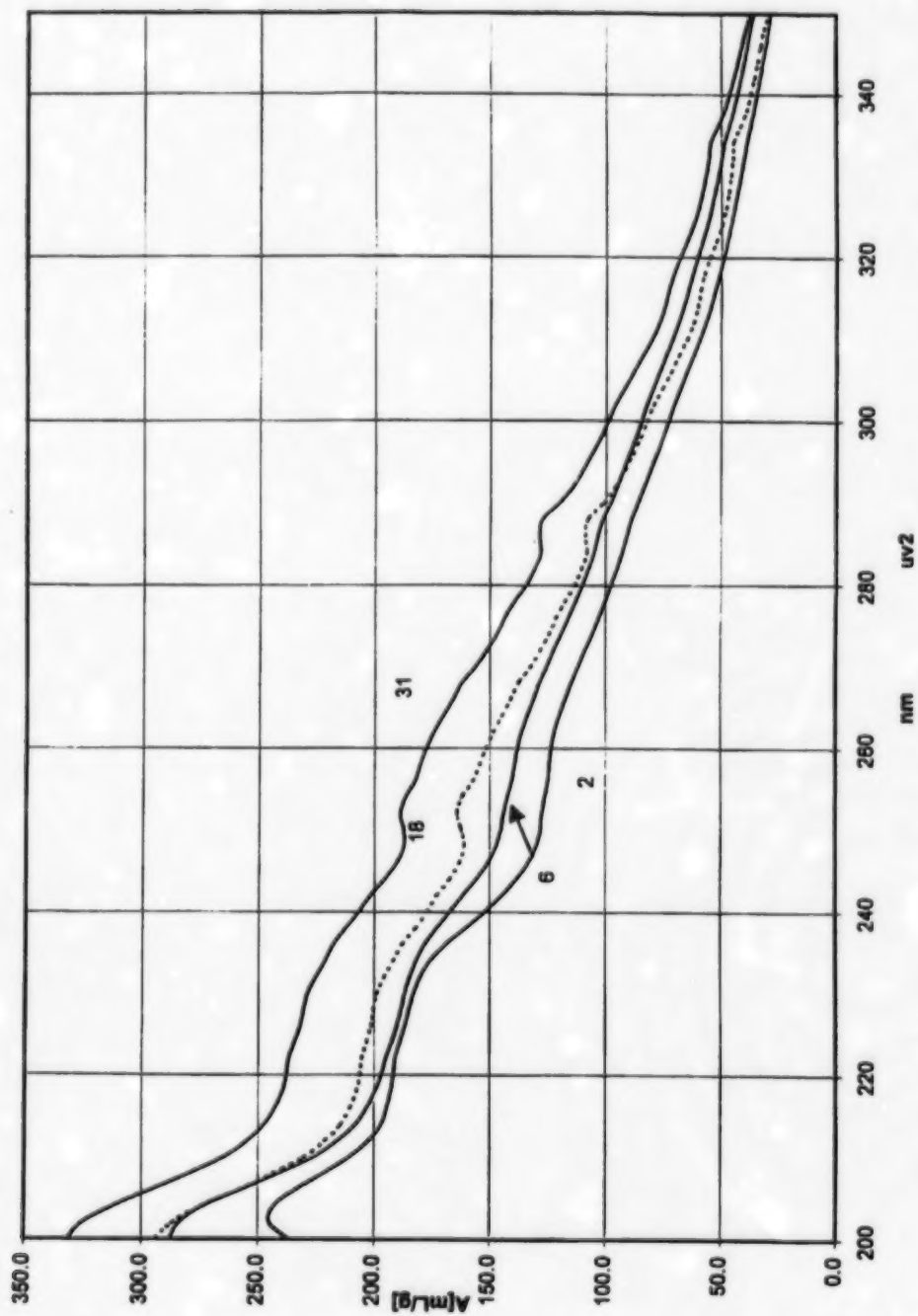


Fig. 3. UV spectra of hexane-soluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

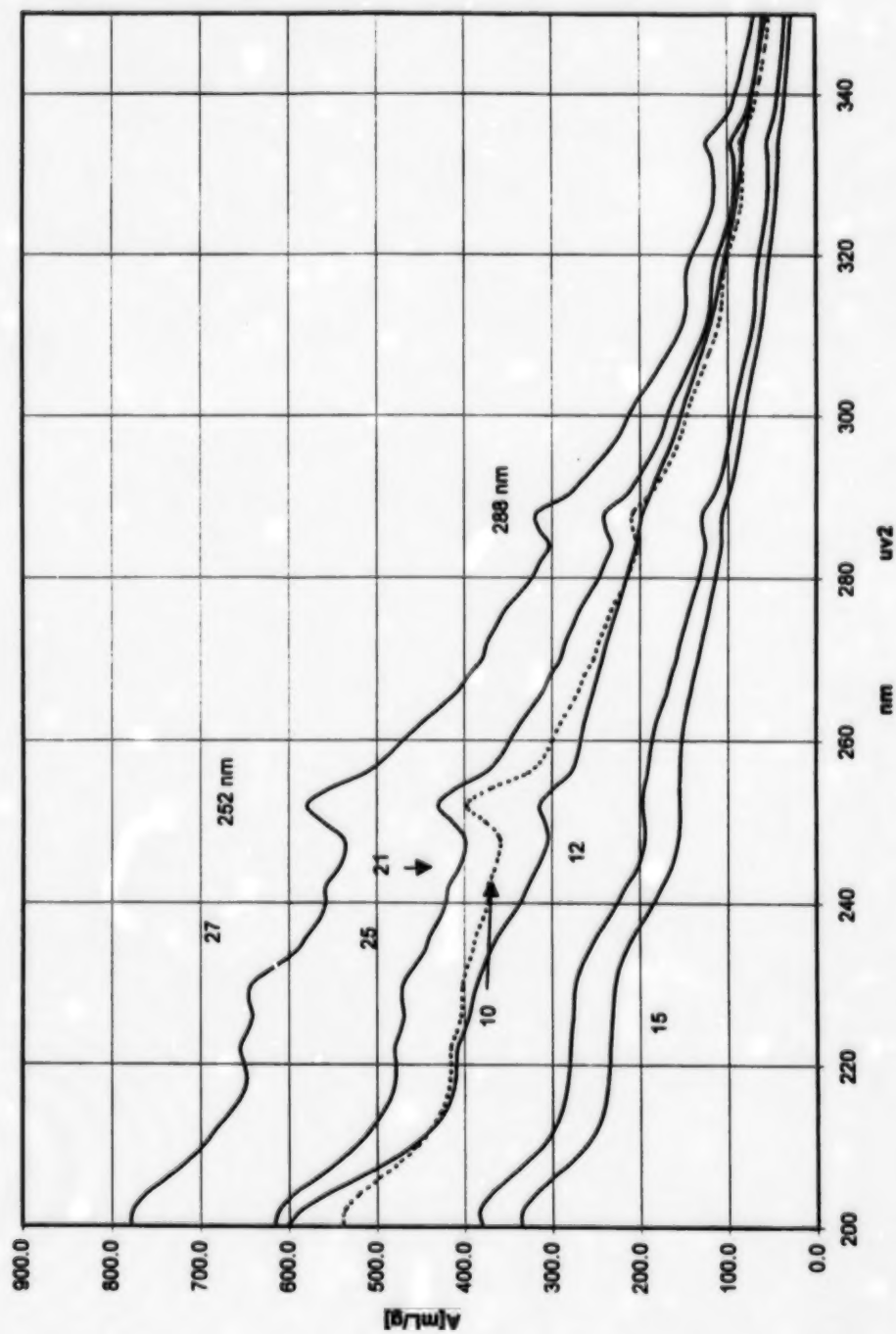


Fig. 4. UV spectra of hexane-soluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

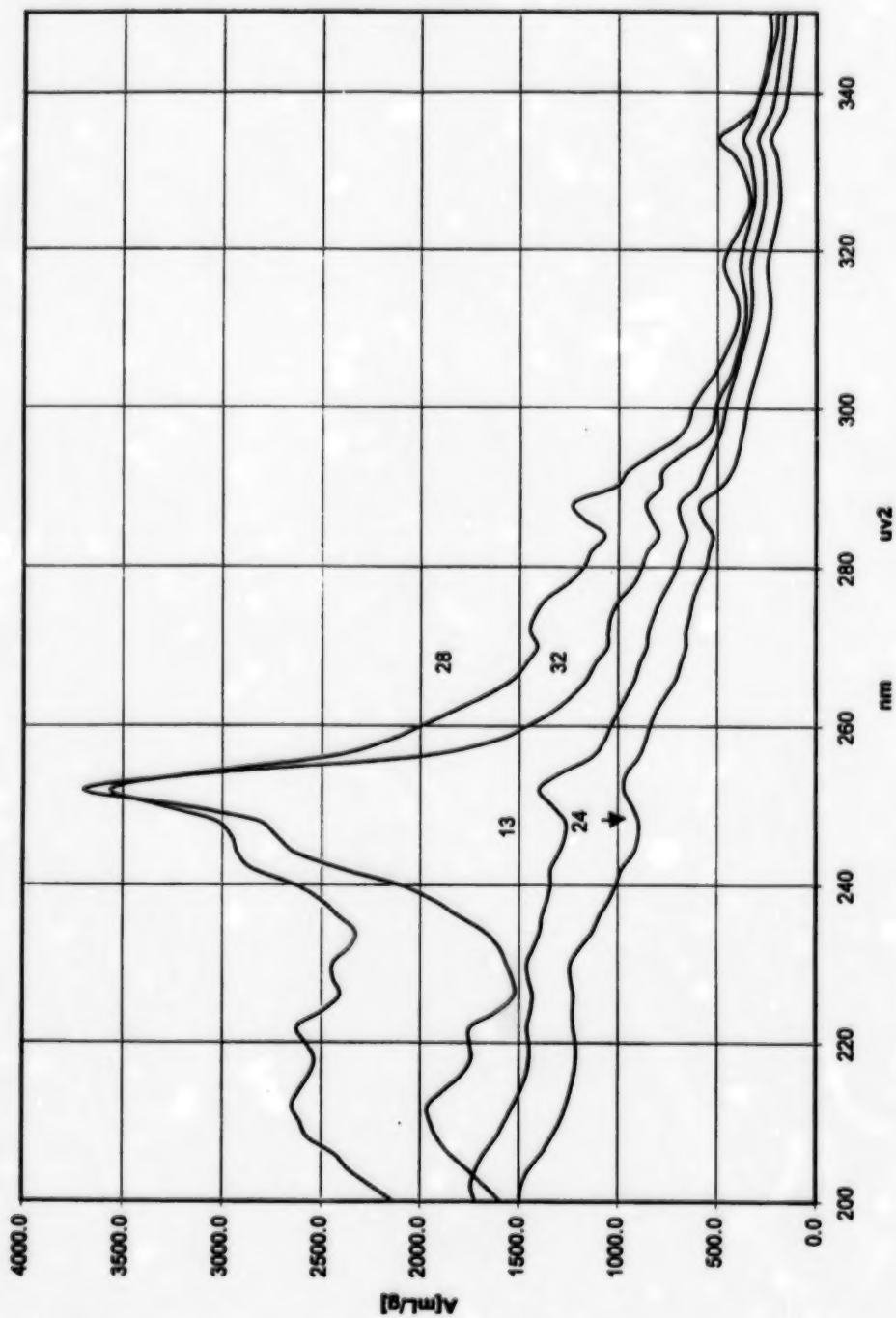


Fig. 5. UV spectra of hexane-soluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table I for sample characteristics and Appendix for sample locations.

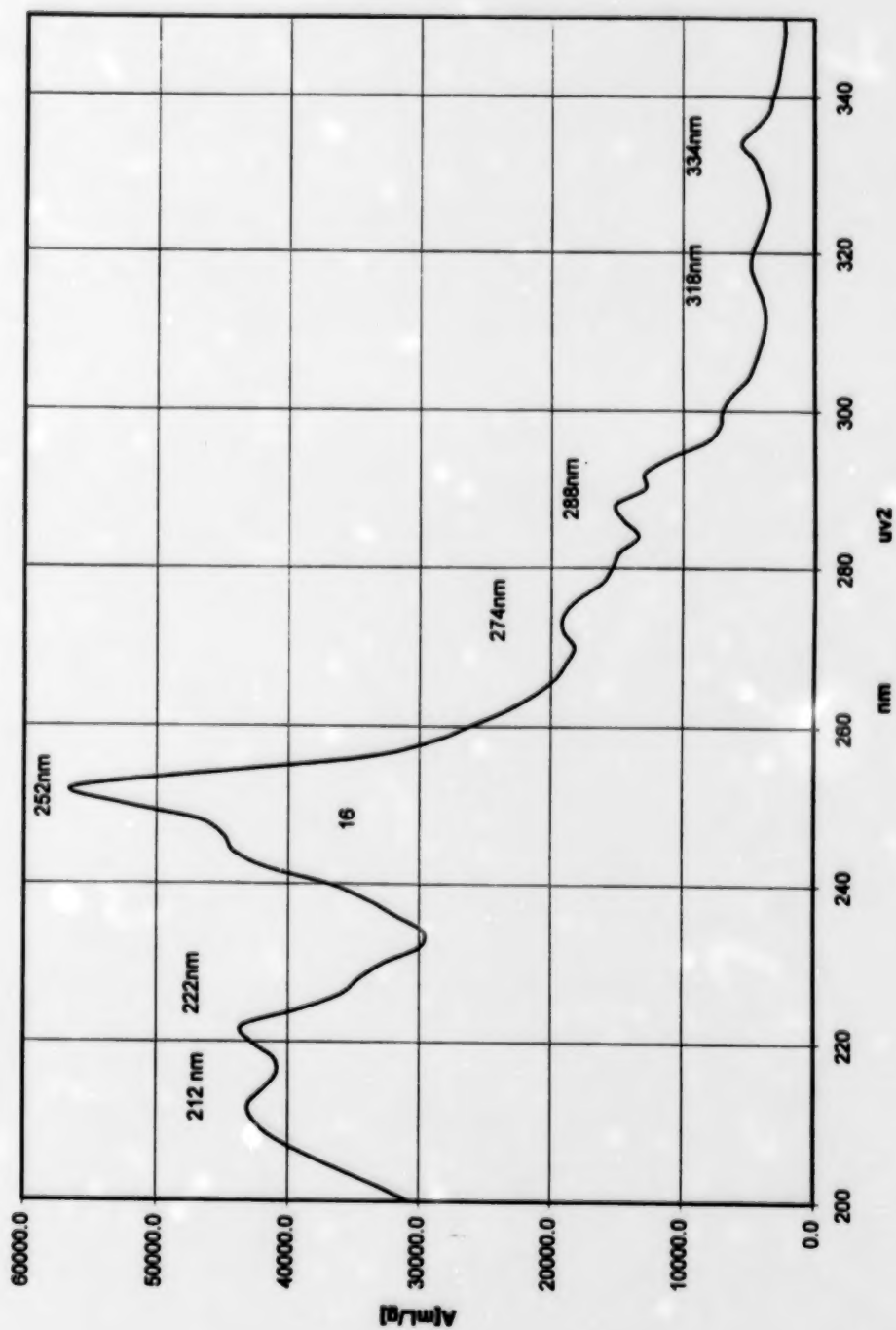


Fig. 6. UV spectra of hexane-soluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

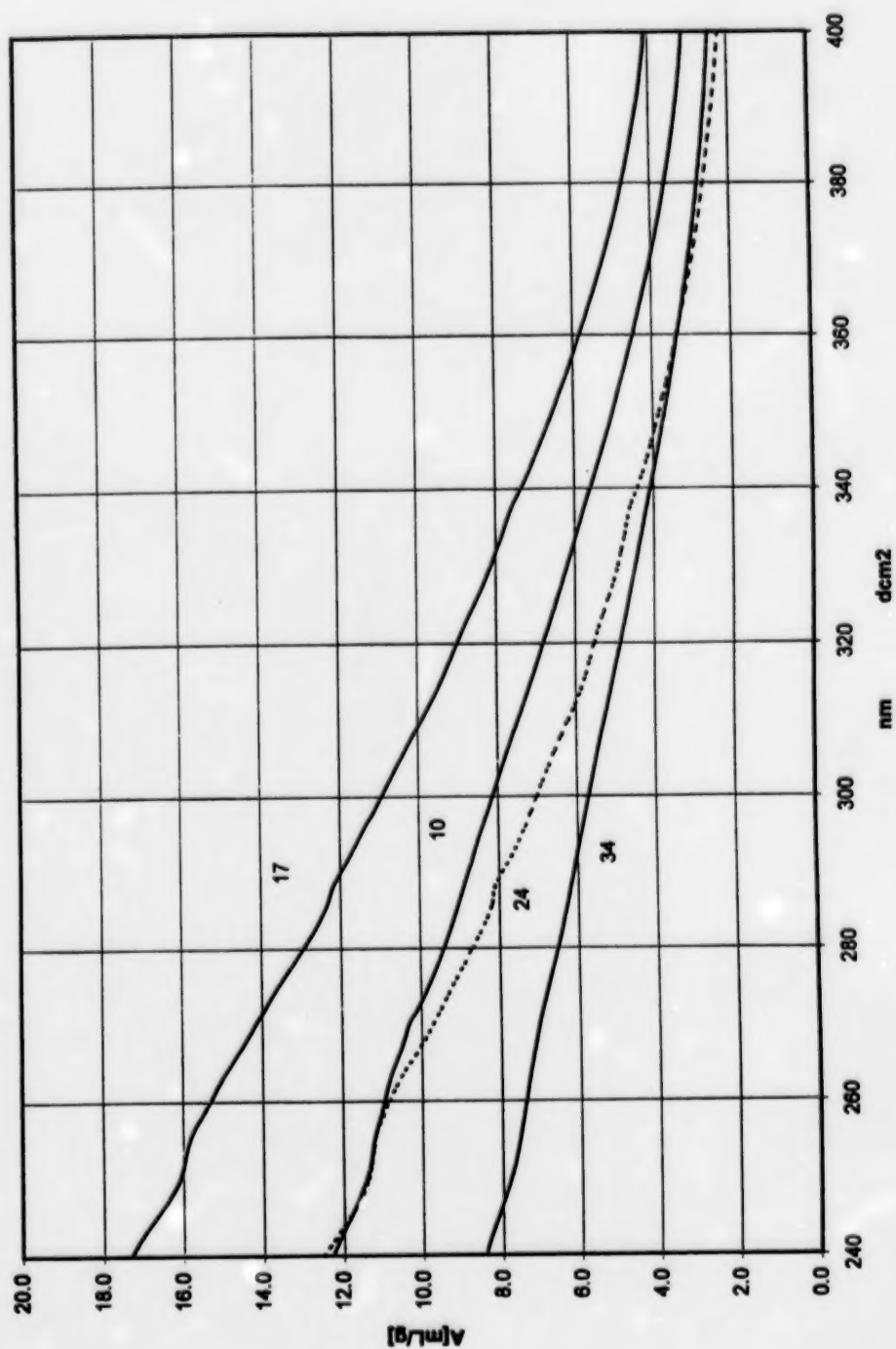


Fig. 7. UV spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

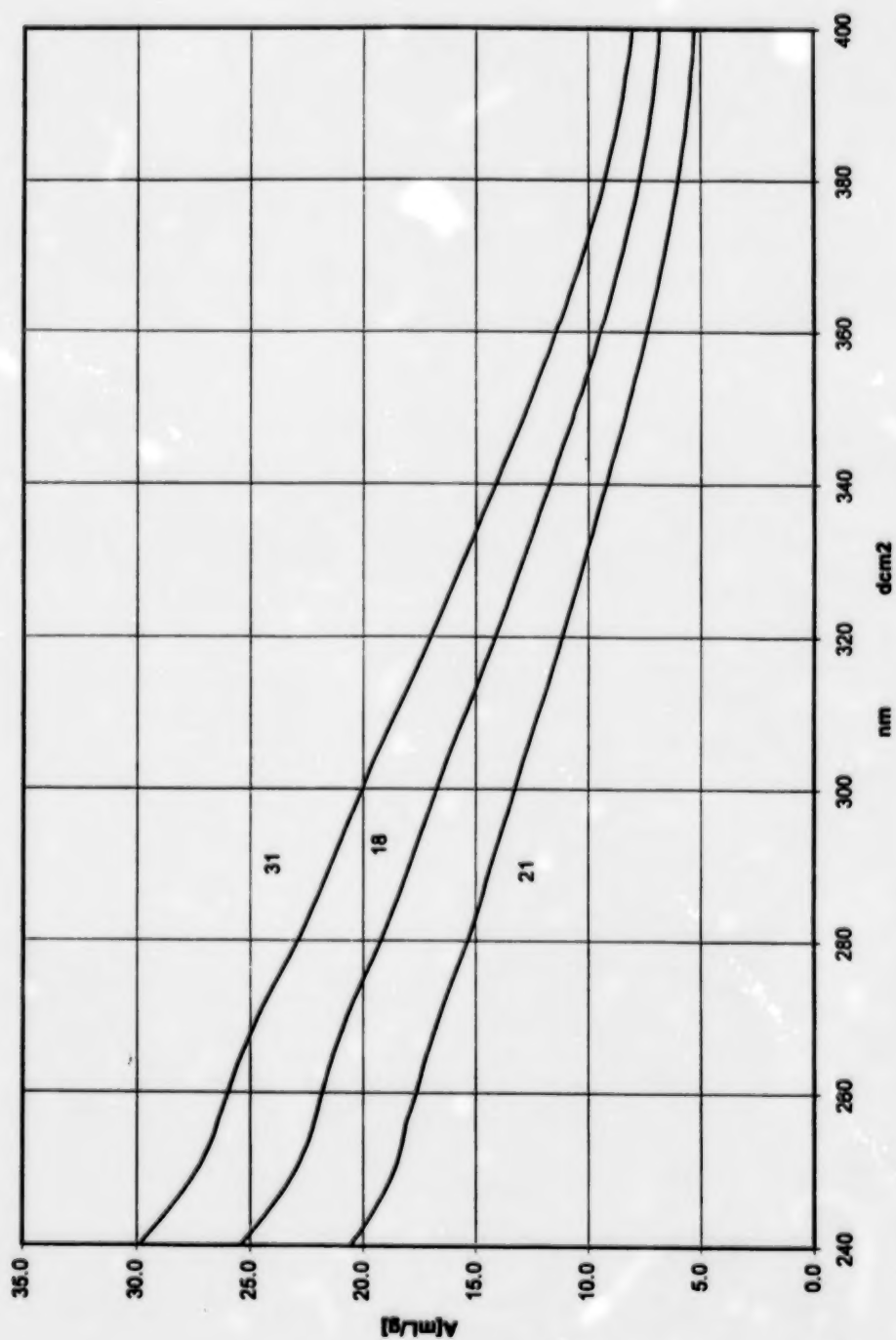


Fig. 8. UV spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table I for sample characteristics and Appendix for sample locations.

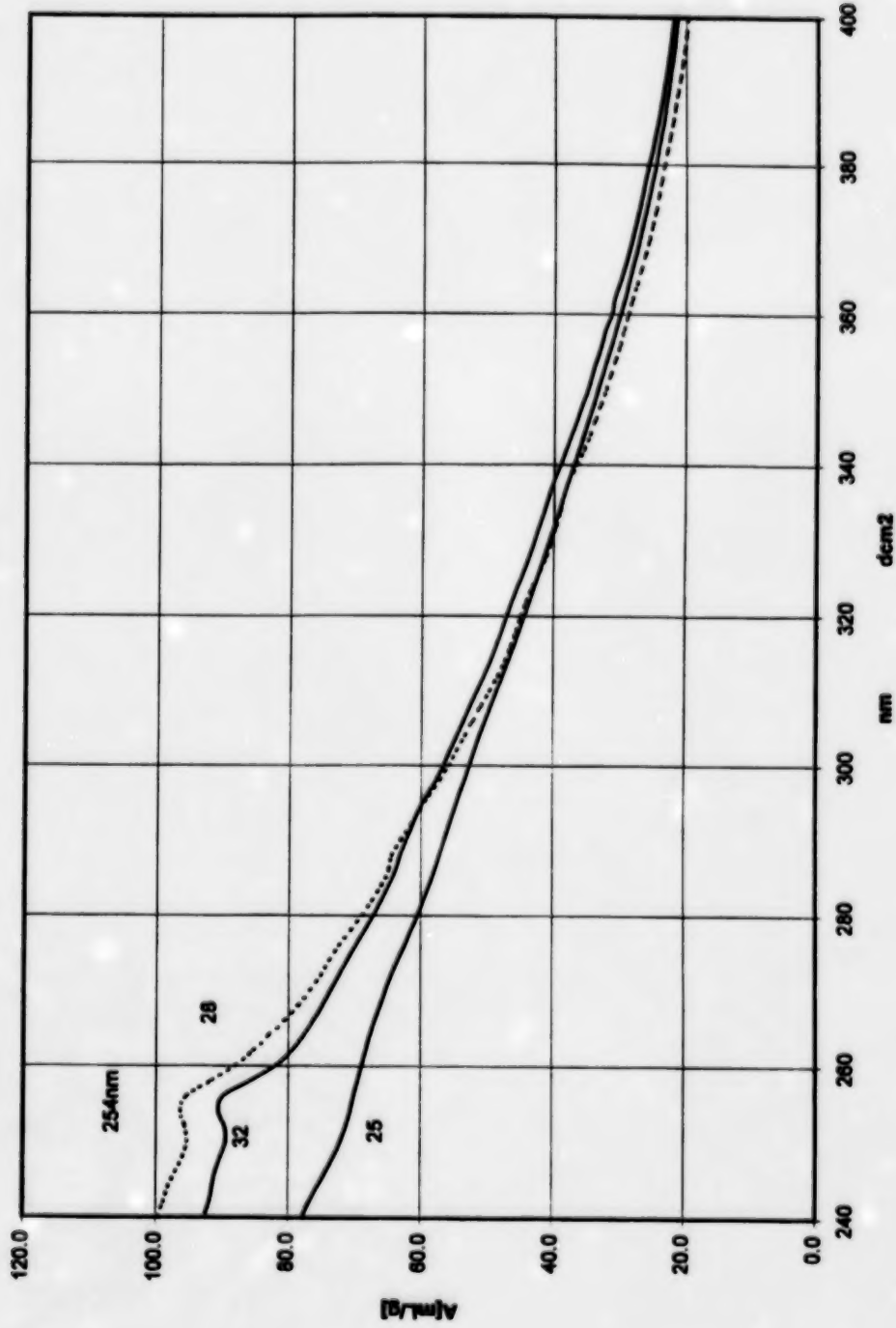


Fig. 9. UV spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

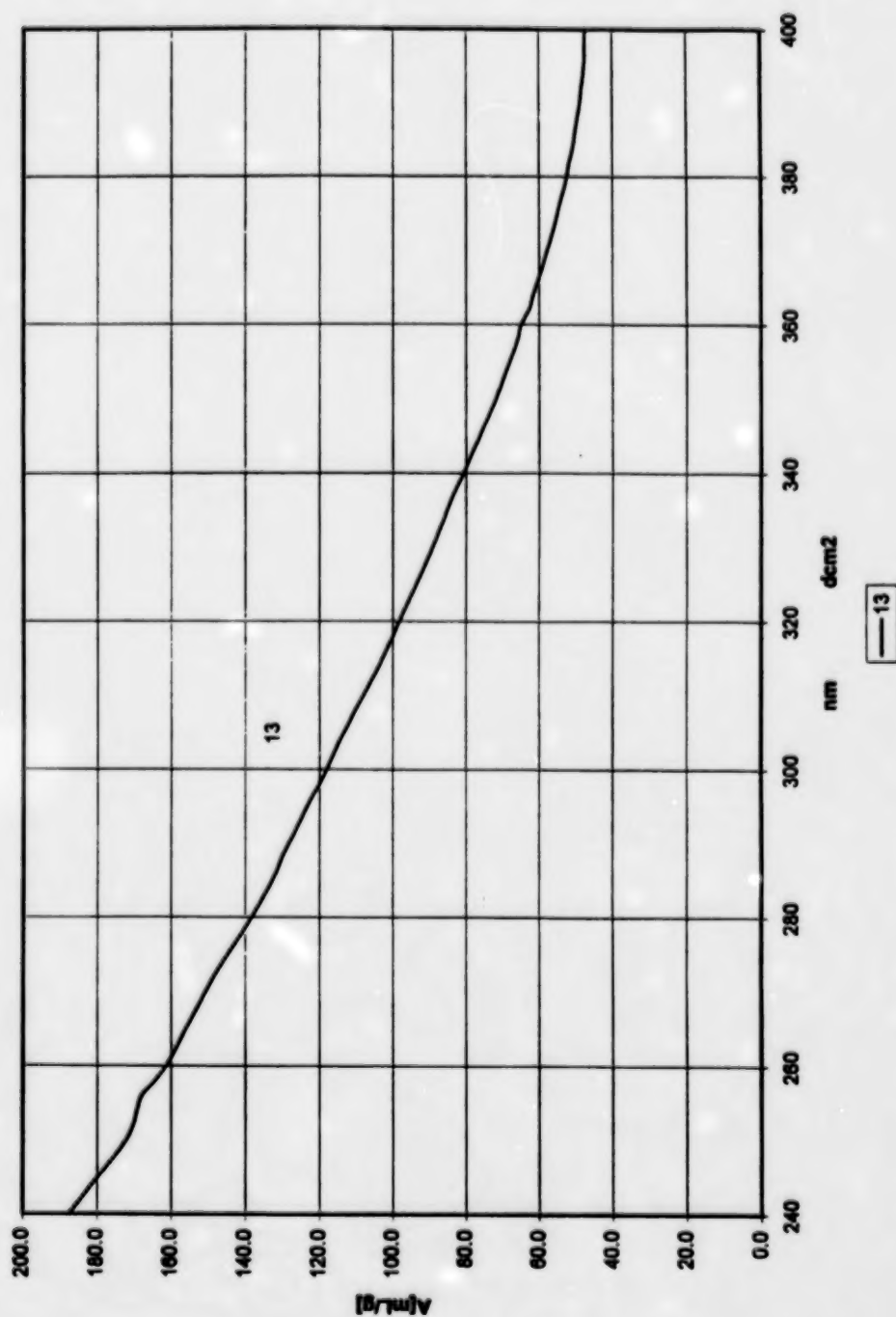


Fig. 10. UV spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

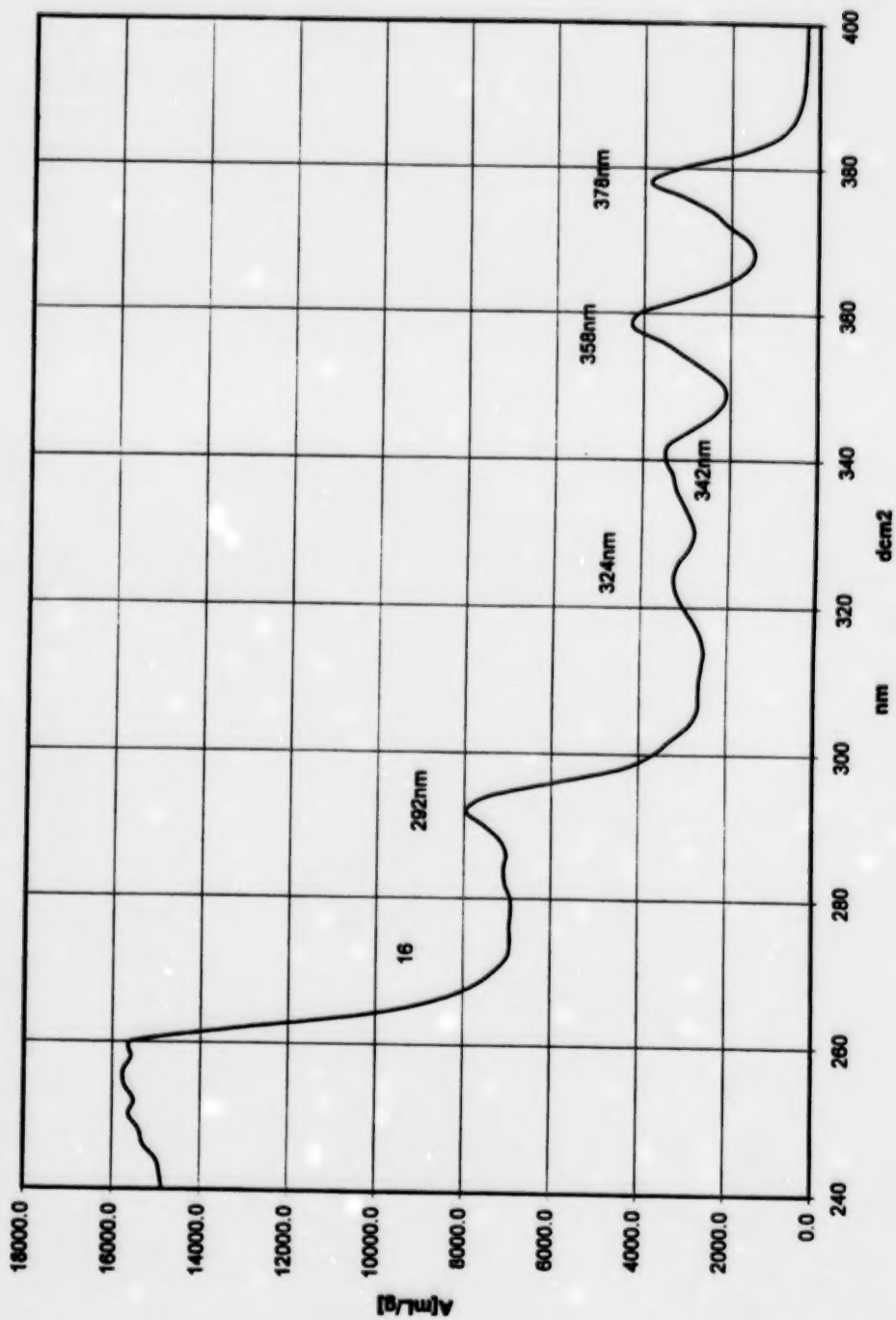


Fig. 11. UV spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

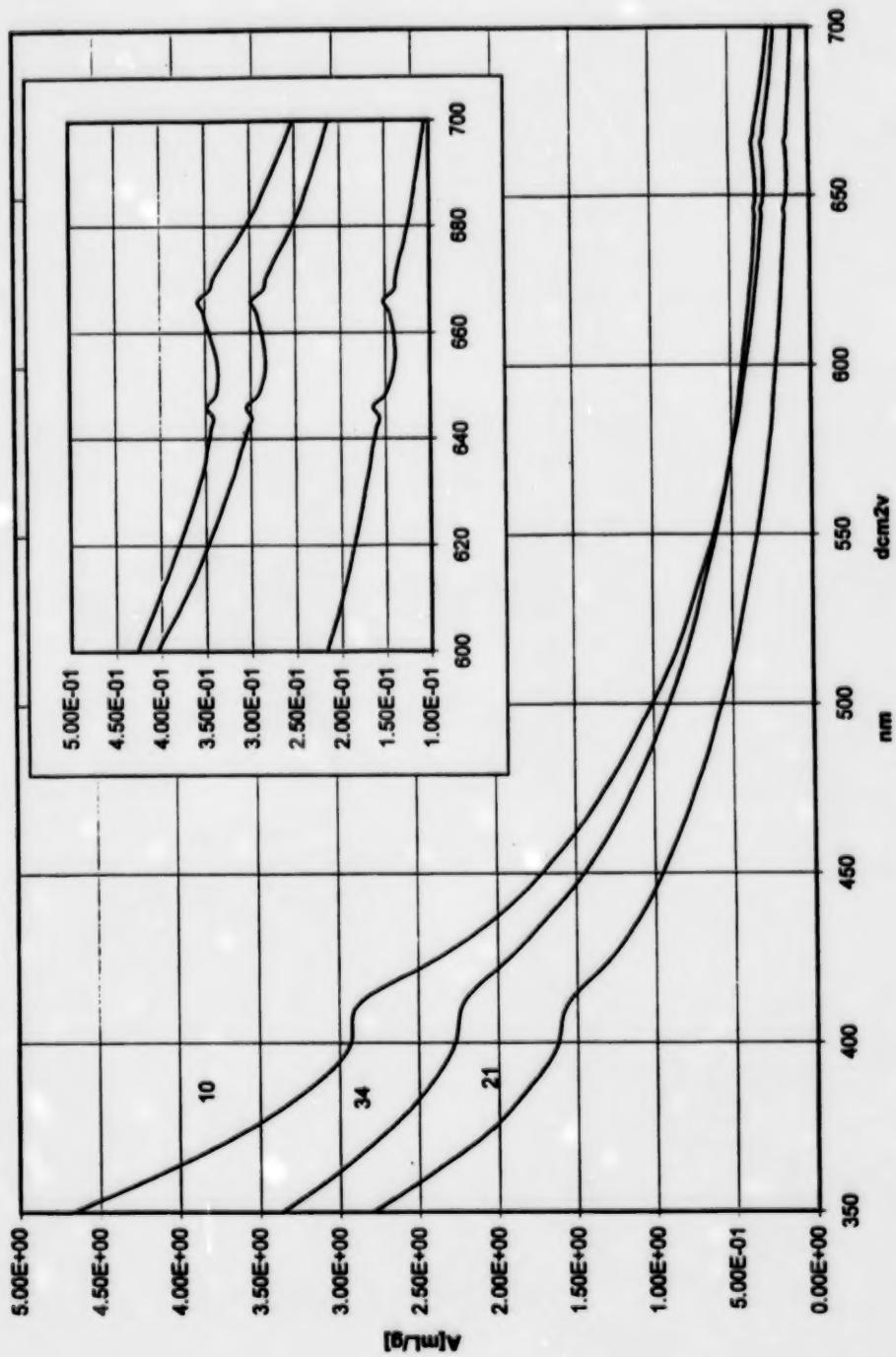


Fig. 12. Visible spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations. Insert is enlarged section of the spectra showing chlorophyll absorption maxima.

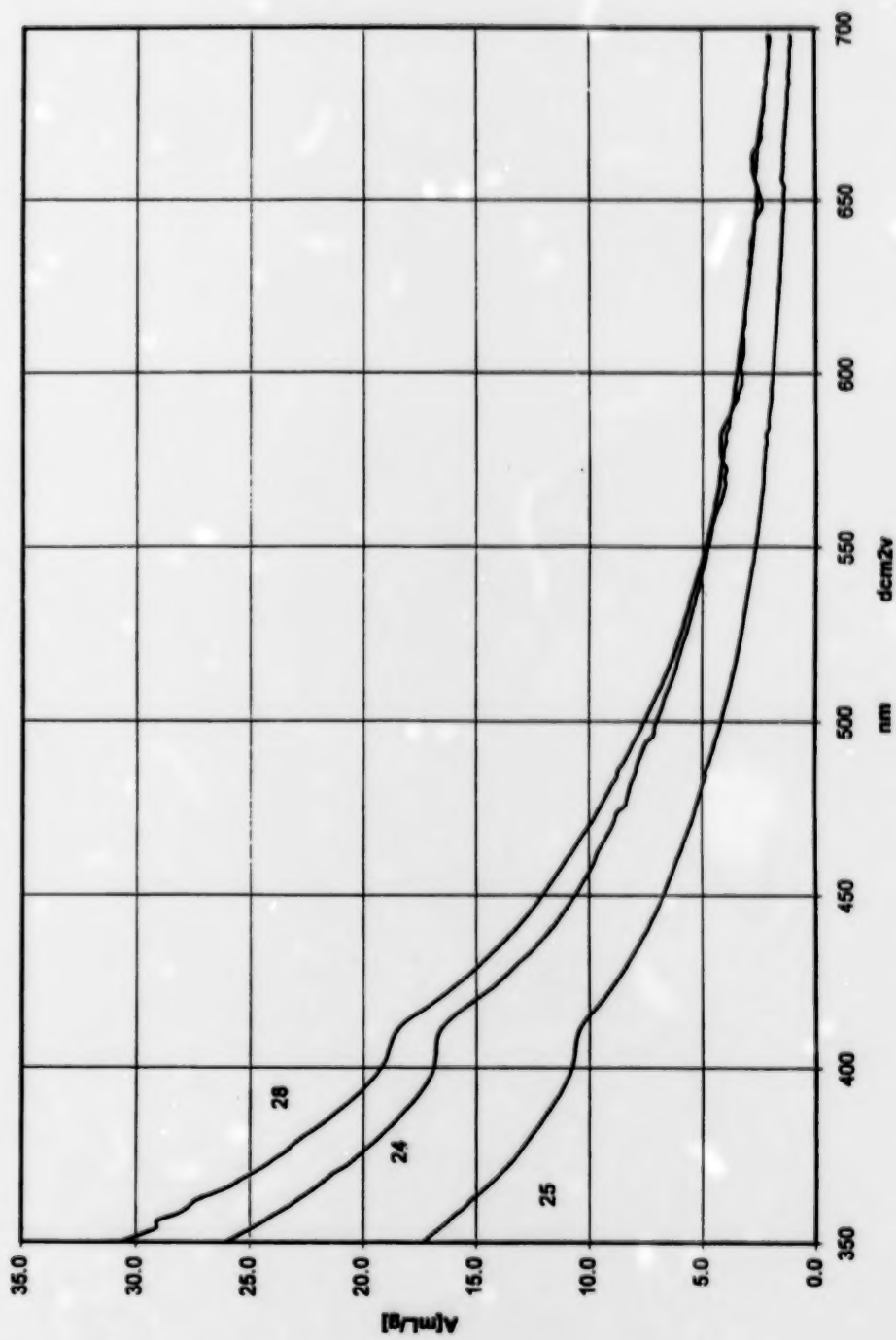


Fig. 13. Visible spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

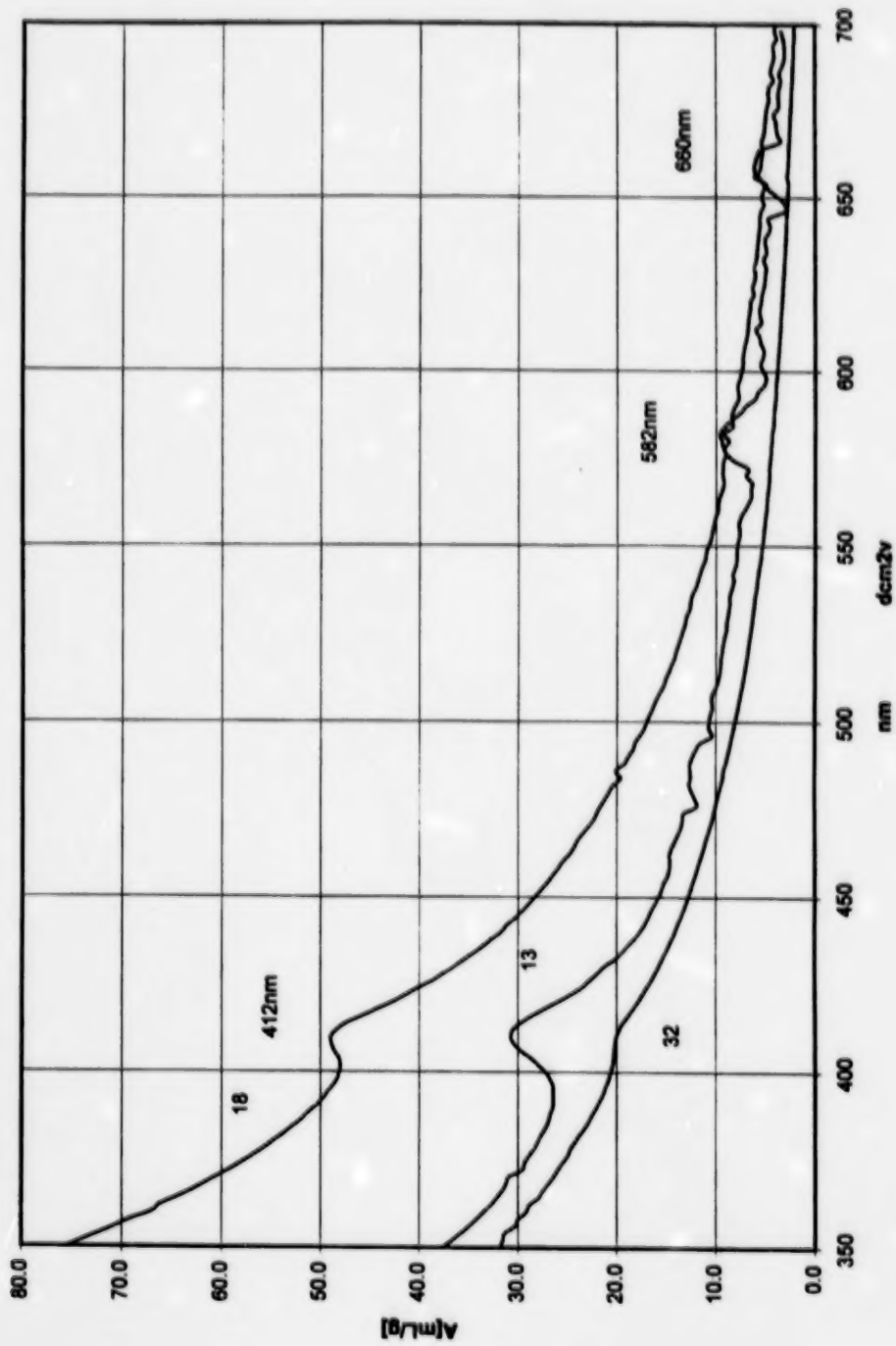


Fig. 14. Visible spectra of hexane-insoluble fractions of dichloromethane extracts of Marsh Creek sediments. See Table 1 for sample characteristics and Appendix for sample locations.

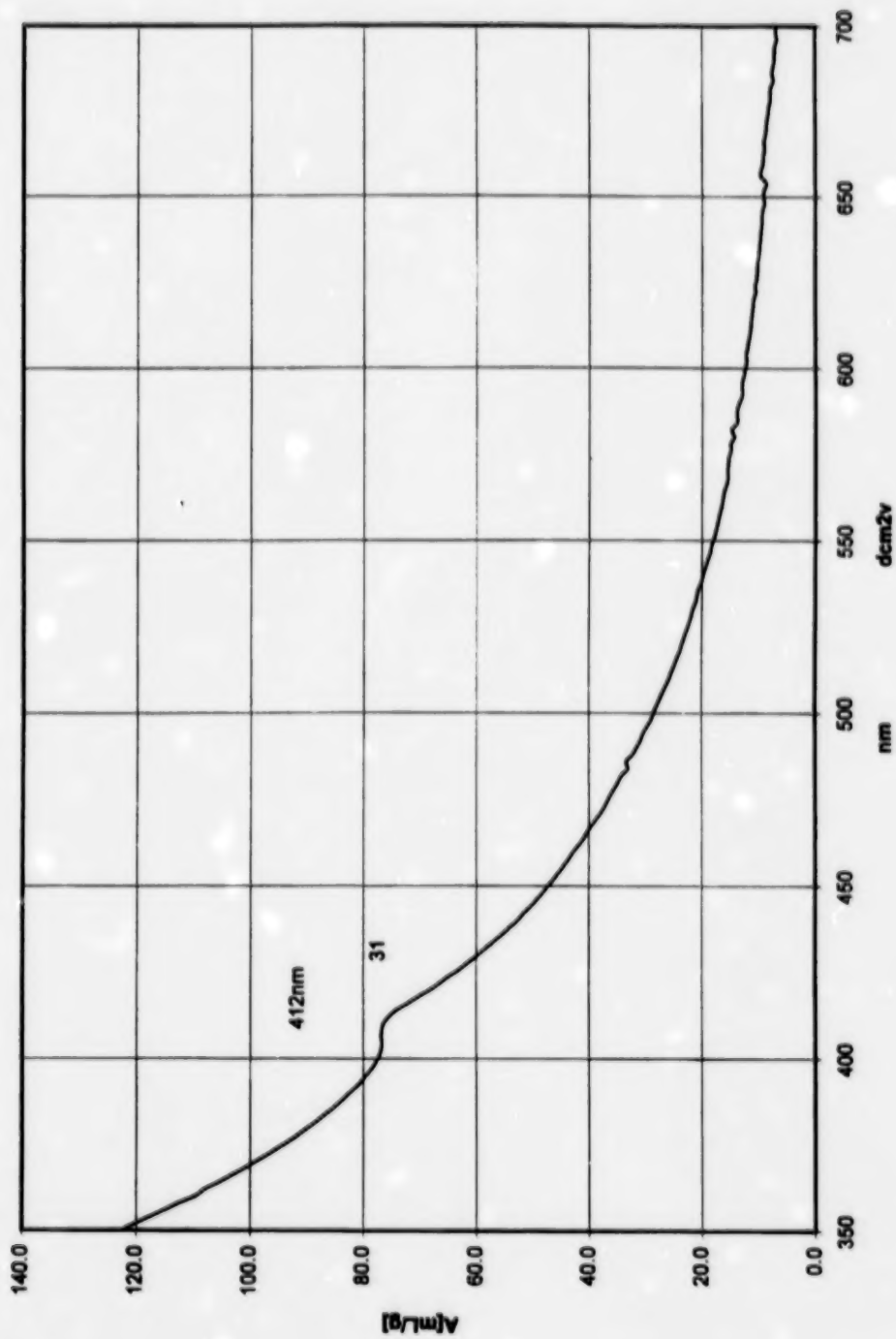


Fig. 15. Visible spectrum of a hexane-insoluble fraction of dichloromethane extract of Marsh Creek sediment. See Table 1 for sample characteristic and Appendix for sample location.

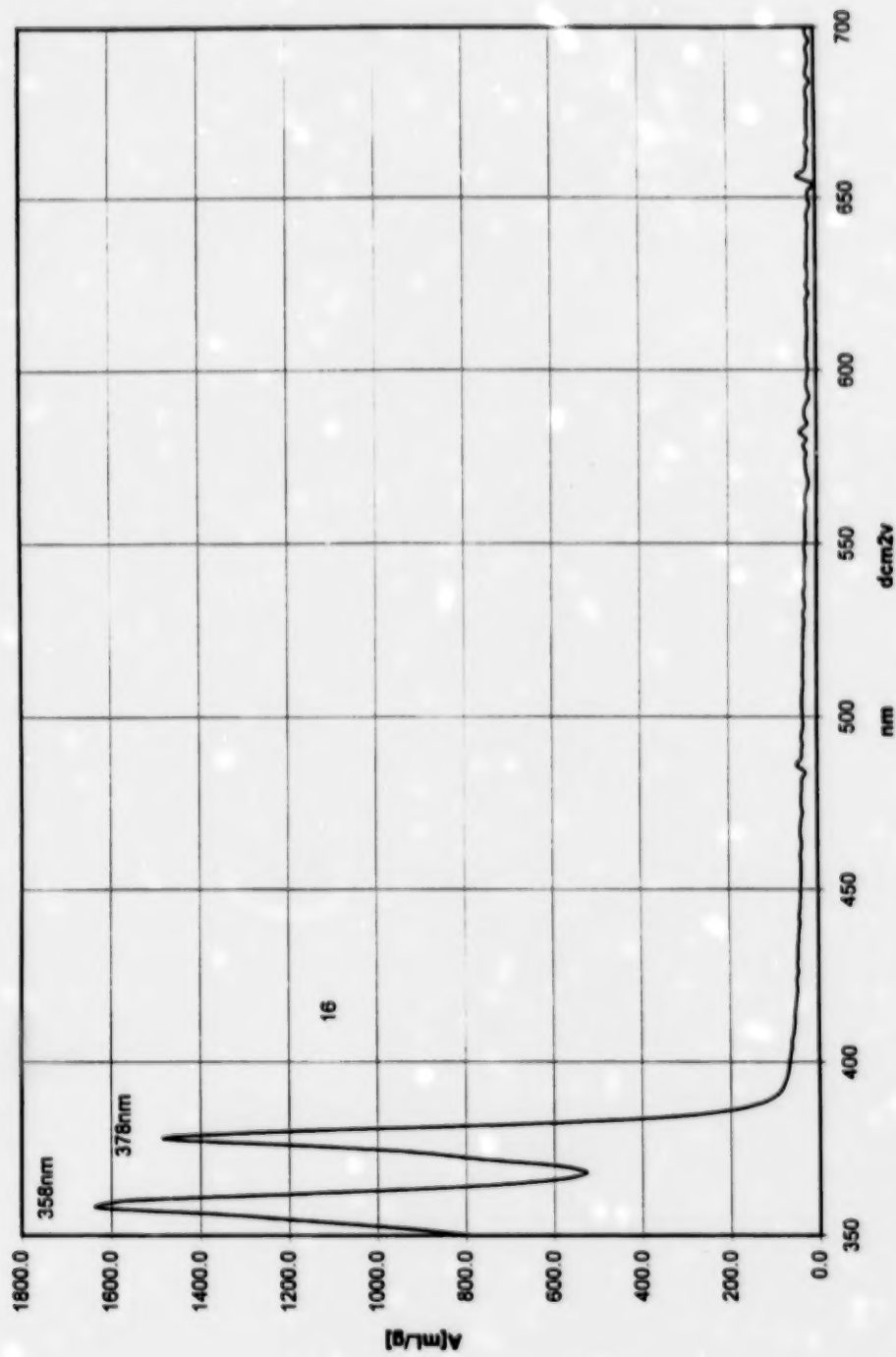


Fig. 16. Visible spectrum of a hexane-insoluble fraction of dichloromethane extract of Marsh Creek sediment. See Table 1 for sample characteristic and Appendix for sample location.

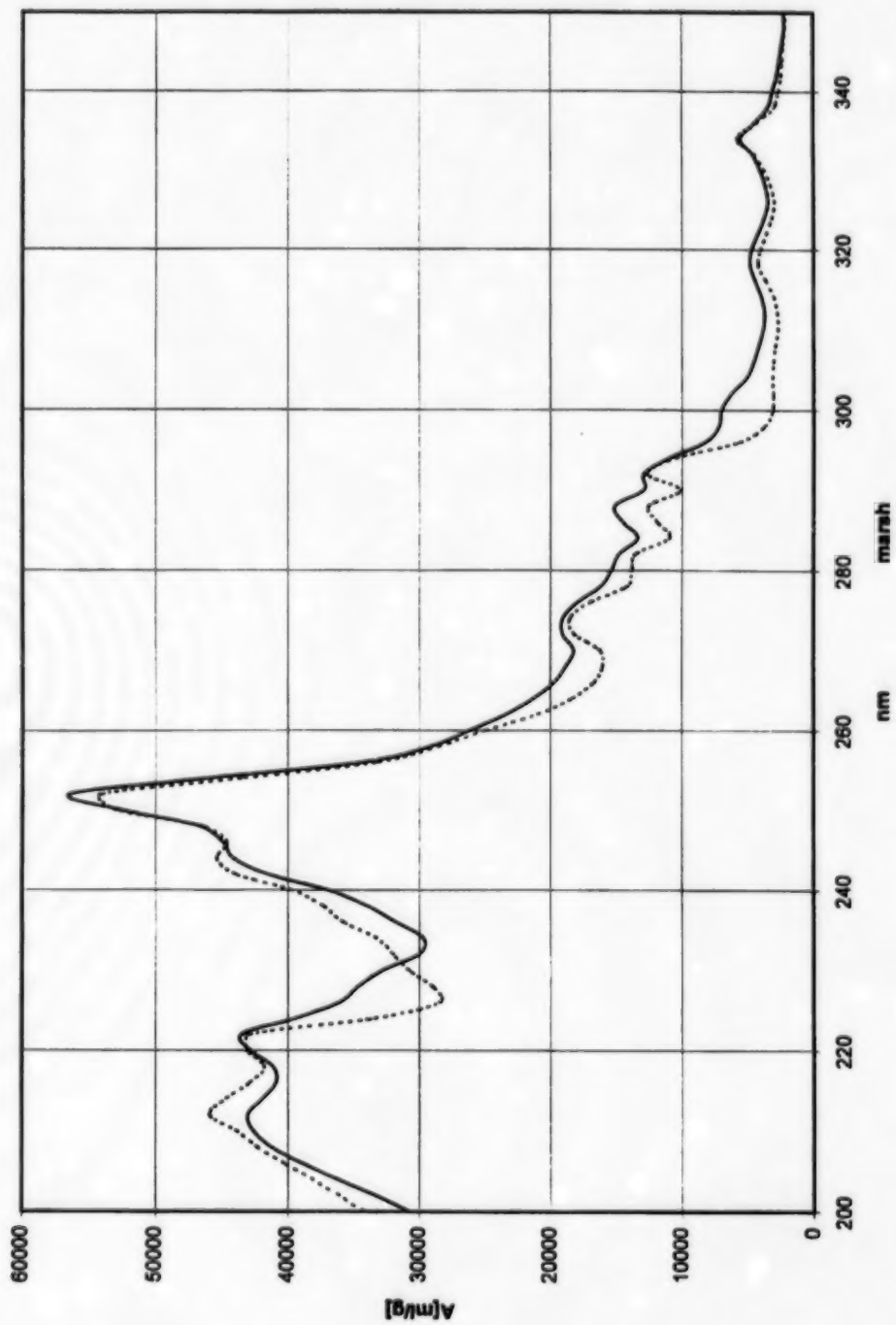


Fig. 17. UV spectrum of hexane-soluble fraction of dichloromethane extract of sample 16 and its approximation by a mixture of naphthalene, phenanthrene, fluoranthene, pyrene, and diesel oil (dotted line).

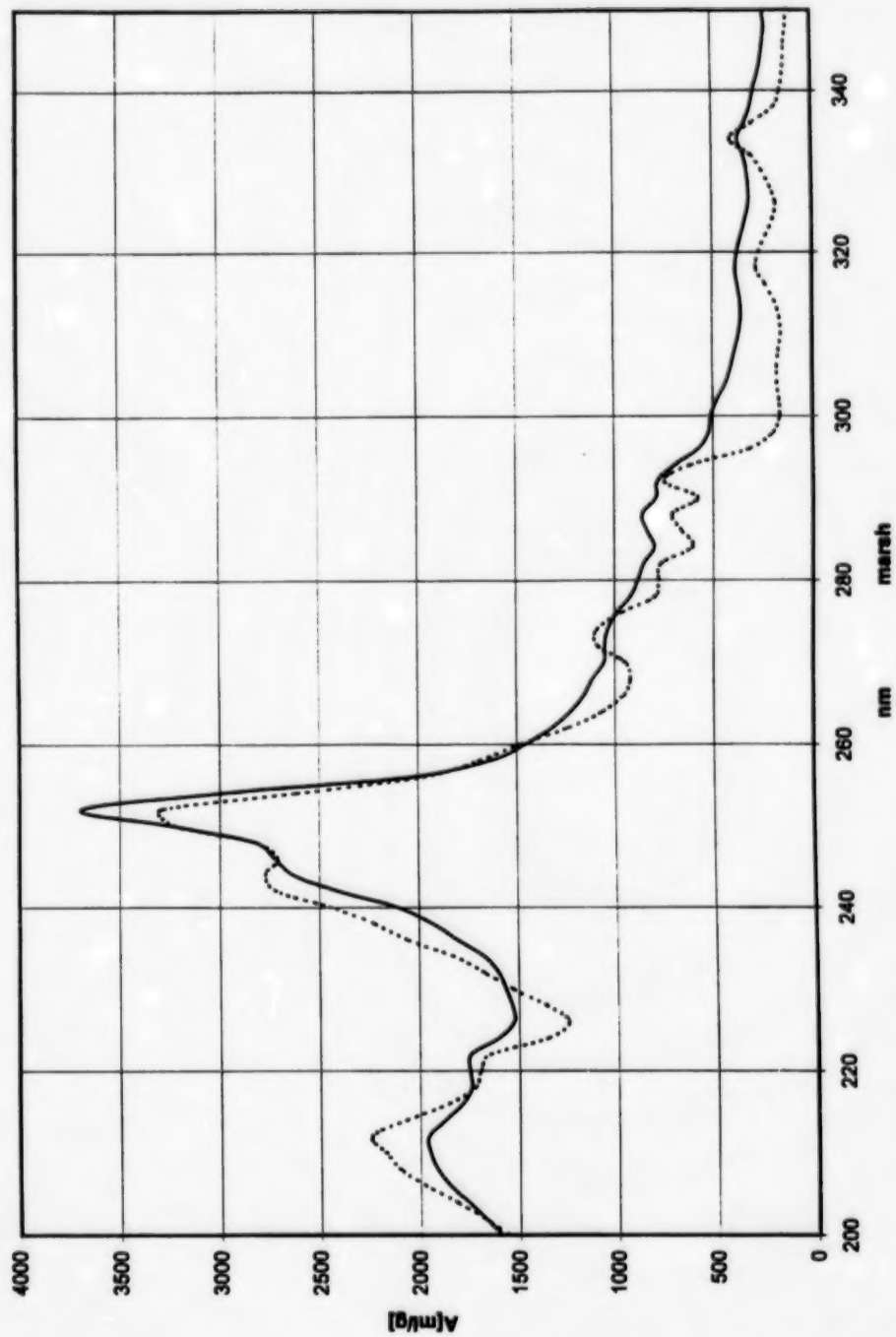


Fig. 18. UV spectrum of hexane-soluble fraction of dichloromethane extract of sample 32 and its approximation by a mixture of naphthalene, phenanthrene, fluoranthene, pyrene, and diesel oil (dotted line).

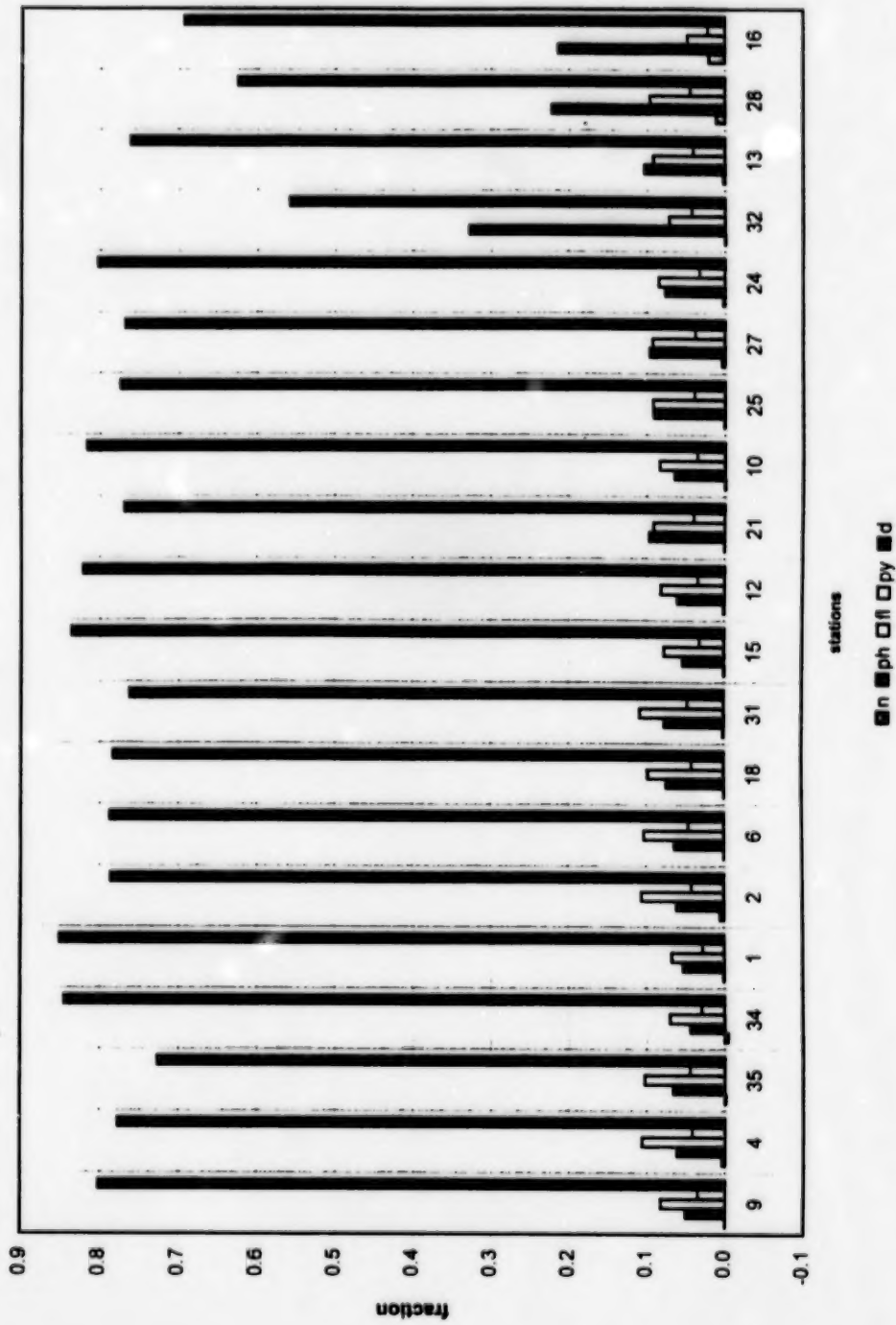


Fig. 19. Proportions of naphthalene, phenanthrene, fluoranthene, pyrene, and diesel oil, approximating spectra of hexane-soluble fractions of dichloromethane extracts.

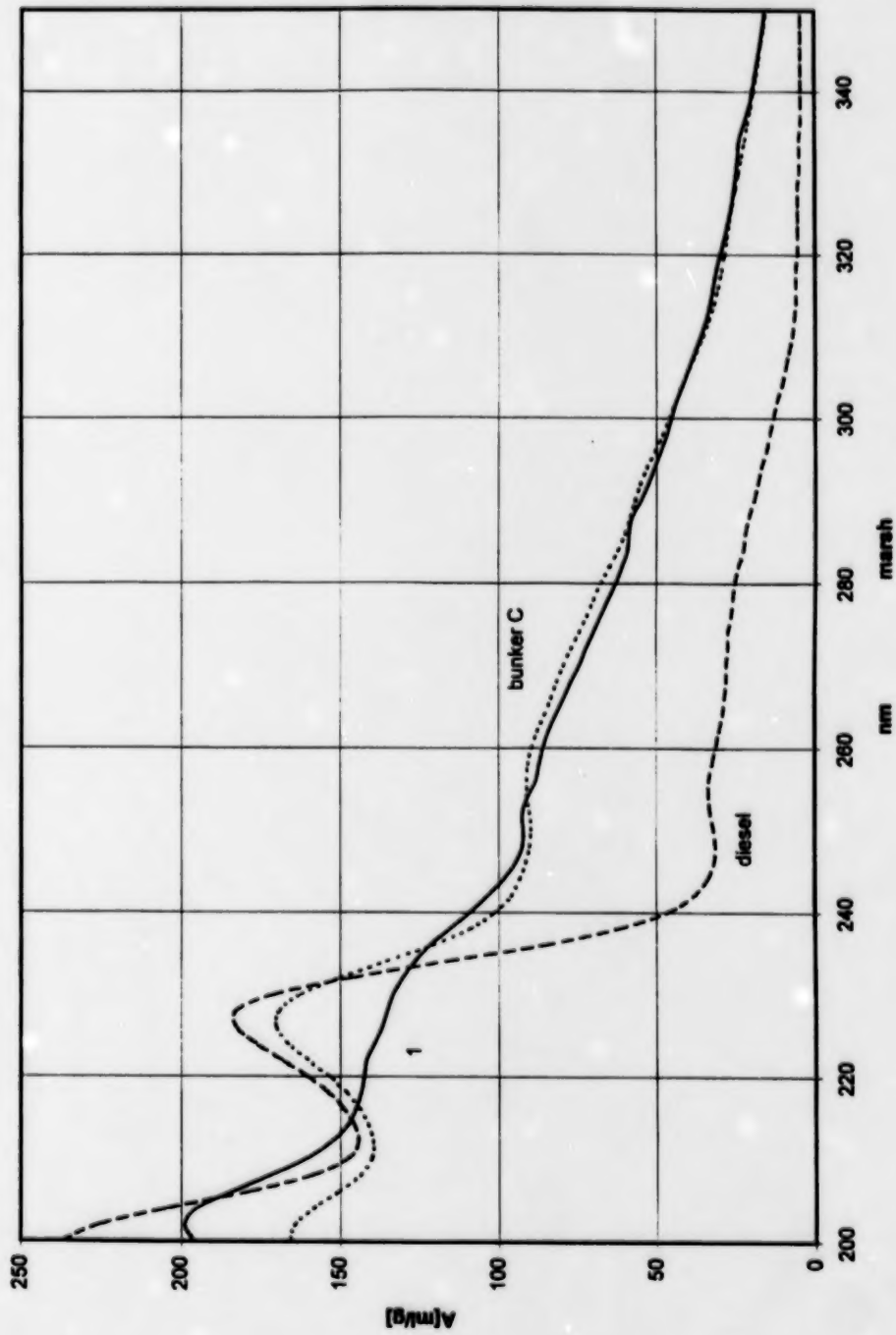


Fig. 20. The approximation of a relatively featureless spectrum of the hexane-soluble fraction of the dichloromethane extract of sample 1 by bunker C and by diesel oil.

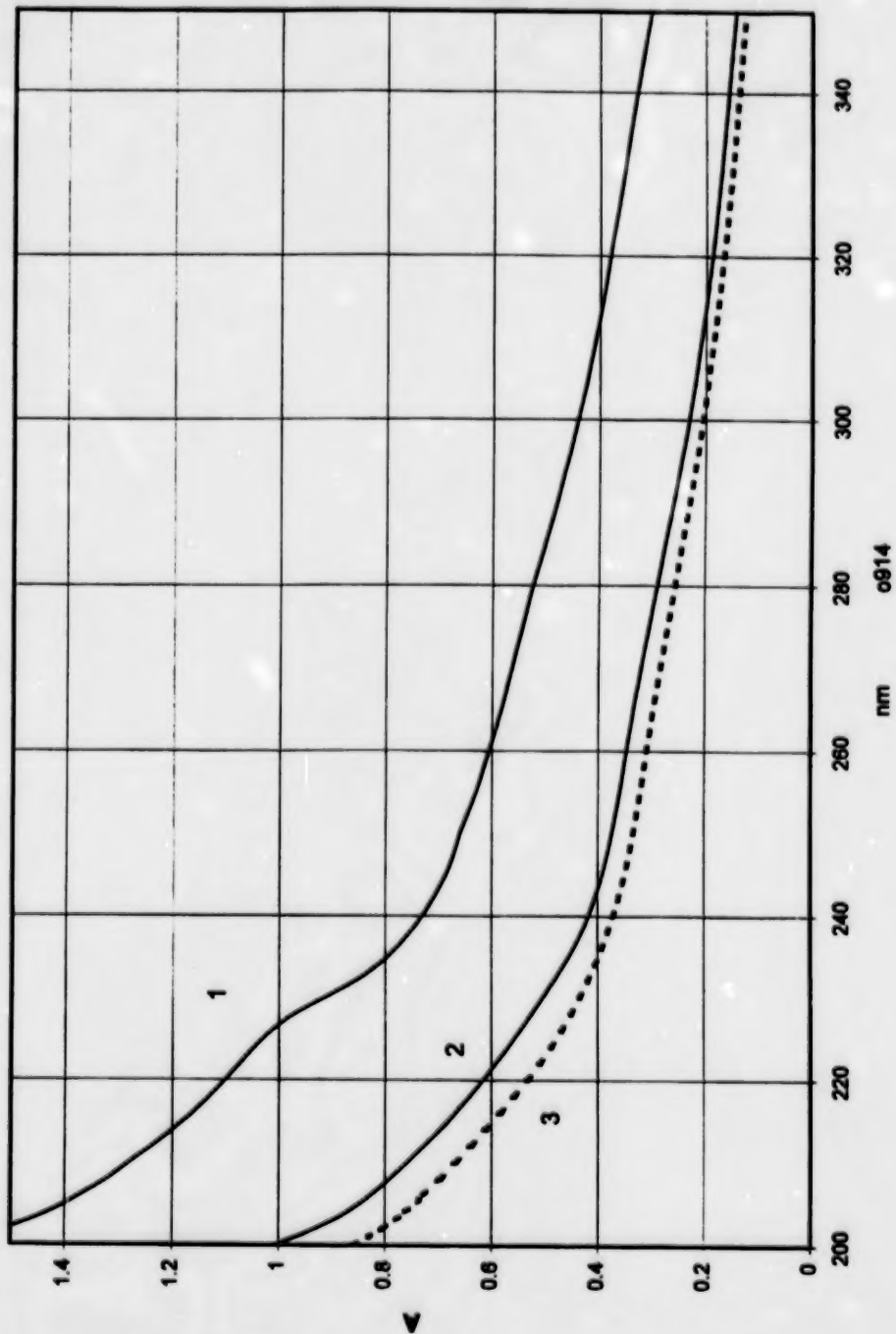


Fig. 21. UV spectra of water samples from interceptor wells (1), and from Marsh Creek downstream (2) and upstream (3) of the contaminated area.

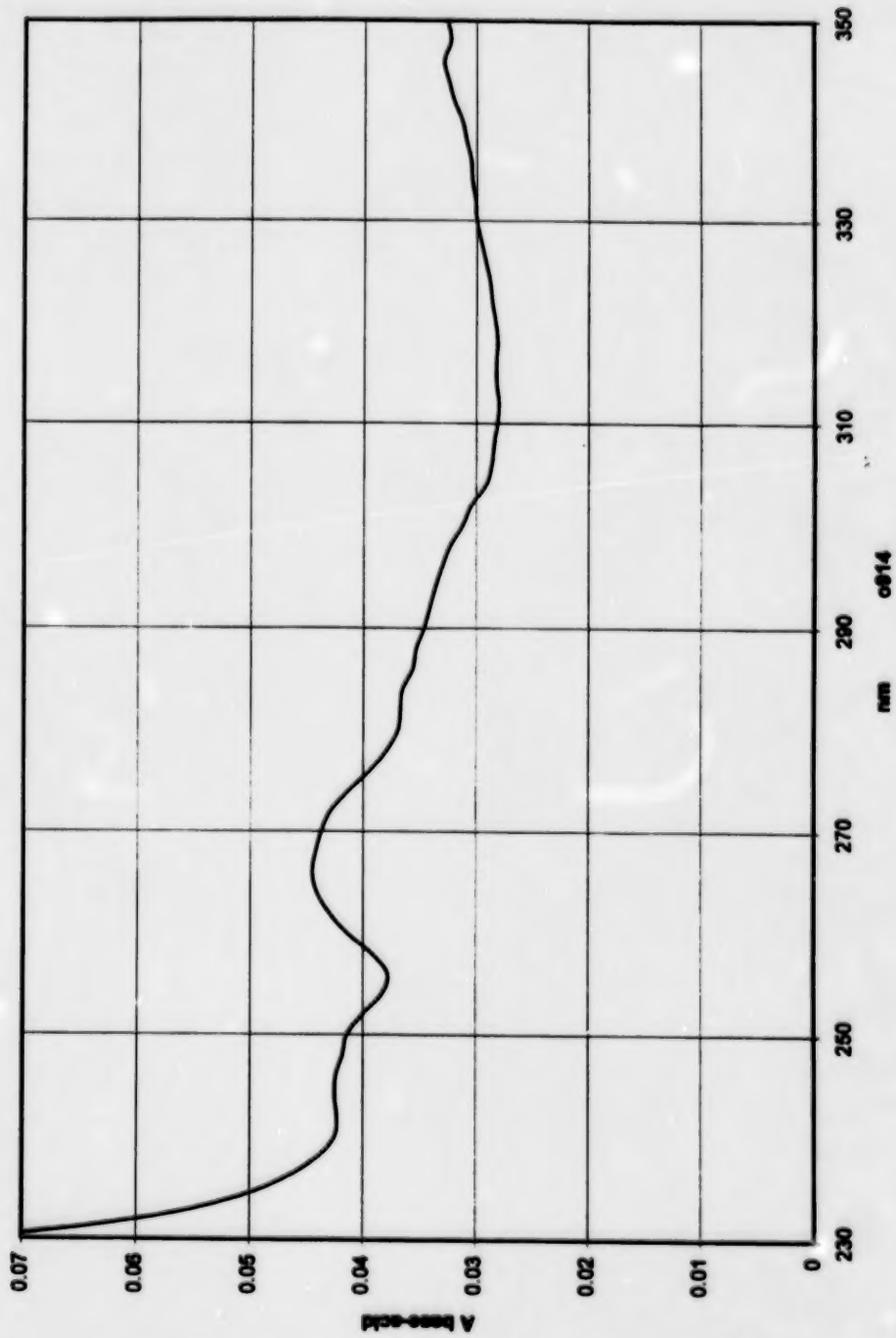


Fig. 22. Difference spectrum (alkaline - acidic) of interceptor well water.

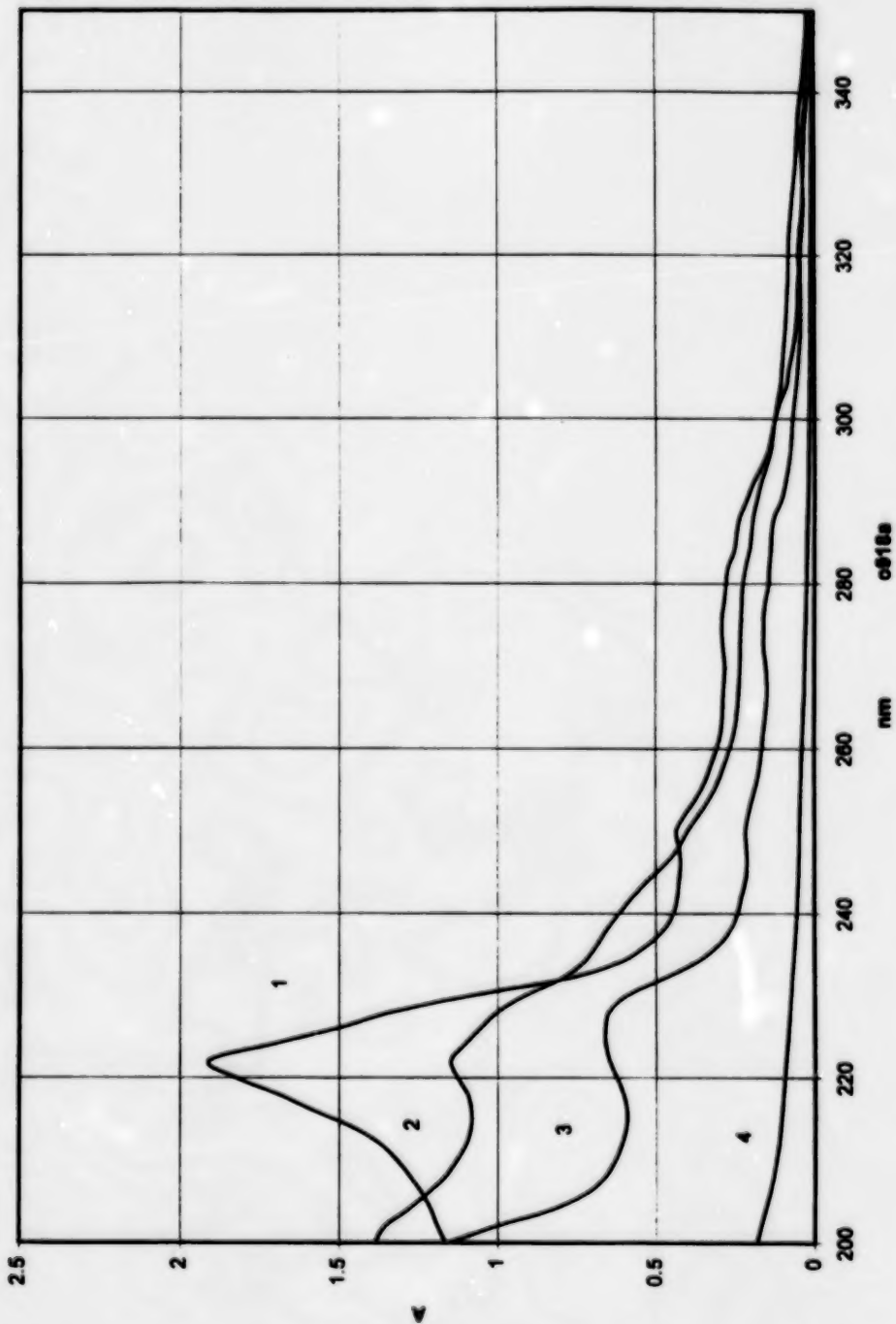


Fig. 23. UV spectra of hexane extracts of interceptor well water as such (1), after acidification (2), Marsh Creek water downstream (3) and upstream (4) of the contaminated area.

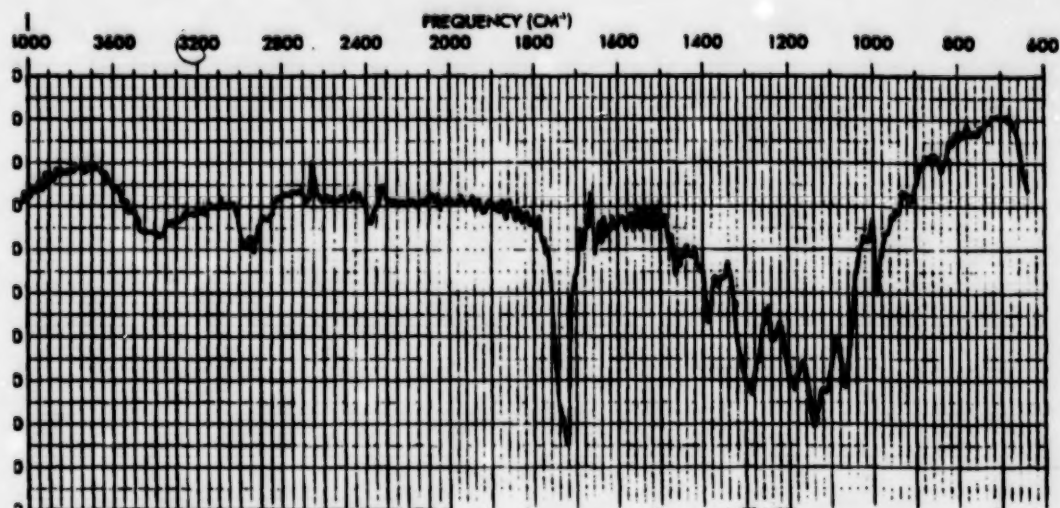


Fig. 24. Infrared spectrum of hexane-insoluble residue after the first dichloromethane extraction.

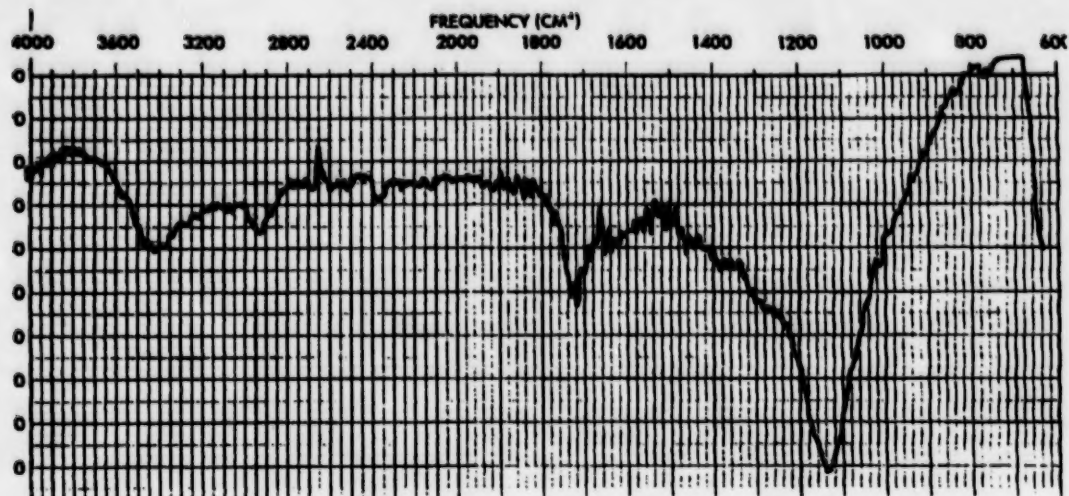


Fig. 25. Infrared spectrum of hexane-insoluble residue after dichloromethane extraction of the acidified sample. Absorption maximum at 1140 cm^{-1} indicates a silicate, but some organics are present as well (maxima at 2940 and 1720 cm^{-1}).

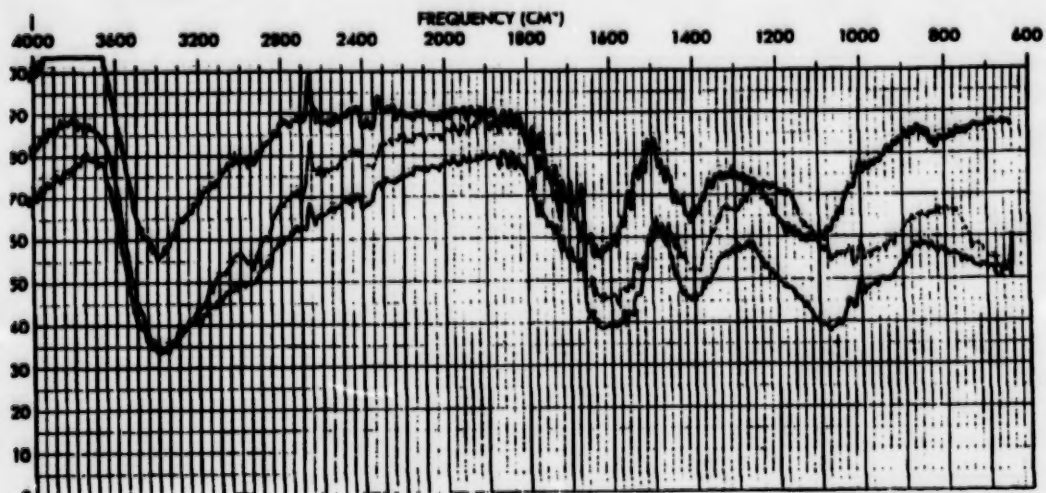


Fig. 26. Infrared spectra of high molecular weight (>1000 dalton) fractions of the effluent and of the interphase formed during the first dichloromethane extraction. From top, water-soluble fraction (fulvic acid), 'interphase', and the precipitate formed during the dialysis (humic acid), respectively.



Fig. 27. Thin layer chromatography (TLC) plate, developed (from left to right) in benzene. From the top, effluent extracted as such, extract of Marsh Creek sediment at station 16, and effluent extracted after acidification, respectively. Drawn outlines - spots visible by fluorescence quenching, letters - fluorescence, B = Blue, G = Green, LB = light blue, LBG = light blue green. Dark spots detected by Fast Black K Salt, red brown to violet in color. The position of a strongly UV-absorbing spot is indicated by arrow at the top.

Appendix

